6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring 1,3-dichloropropene in environmental media and in biological samples. The intent is not to provide an exhaustive list of analytical methods that could be used to detect and quantify 1,3-dichloropropene. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to detect 1,3-dichloropropene in environmental samples are the methods approved by federal agencies such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that refine previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

6.1 BIOLOGICAL MATERIALS

The available literature produced only one recent method for determining levels of cis- and trans-1,3-dichloropropene in biological materials. Kastl and Hermann (1983) developed an analytical procedure for determining the level of cis- and trans-1,3-dichloropropene in whole rat blood. Blood is extracted, 200 µL n-hexane is added, and the sample is vortexed and centrifuged at 800 g for 1 minute. Samples are either directly injected onto a GC column for GC/MS analysis or diluted with hexane for GC/ECD (electron capture detection) analysis. Percent recoveries of the GC analysis range from 80.8 to 98.5 for the cis isomer and 81.3 to 98.2 for trans.-1,3-dichloropropene. For GC/MS analysis, percent recoveries are between 83.1 and 94.9 for cis- and 88.7 and 98.8 for trans-1,3-dichloropropene. The GC/ECD method is sensitive to cis and trans isomeric concentrations in rat blood of $5.88\text{-}1.17\text{x}10^{4}$ and $5.35\text{-}1.07\text{x}10^{4}$ ng/mL, respectively. The GC/MS method is sensitive to cis- and trans-1,3-dichloropropene concentrations in rat blood of $5.18\text{x}10^{1}$ to $1.29\text{x}10^{4}$ and $4.71\text{x}10^{1}$ to $1.18\text{x}10^{4}$ ng/mL, respectively.

Table 6-l summarizes the methods used to detect 1,3-dichloropropene in biological materials, including a procedure for detecting 1,3-dichloropropene in foods (Daft 1989).

In addition, the detection of N-acetyl cysteine conjugate in urine has been used to indicate human exposure to 1,3-dichloropropene (Osterloh et al. 1984, 1989a, 1989b).

6.2 ENVIRONMENTAL SAMPLES

Procedures for detecting cis- and trans-1,3-dichloropropene in water, soil, and sediment samples at hazardous waste sites are outlined in the method for semivolatiles in the CLP Statement of Work for Organics Analysis (EPA 1988). The required quantification limits for both cis- and

TABLE 6-1. Analytical Methods for Determining cis- and trans-1,3-Dichloropropene in Biological Materials

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Rat blood	Extract with hexane vortex and centrifuge	GC/MS	51.8 ng/mL (cis) 4.71 ng/mL (trans)	83.1-94.9 (cis) 88.7-98.8 (trans)	Kastl and Hermann 1983
Rat blood	Extract with hexane vortex and centrifuge	GC/ECD	5.88 ng/mL (cis) 5.35 ng/mL (trans)	80.8-98.5 (cis) 81.3-98.2 (trans)	Kastl and Hermann 1983
Food	Extract composited, table-ready foods with isooctane or acetone-aqueous phosphoric acid-isooctane mixture	GC-ECD/HECD	No data	45-112	Daft 1989

ECD = electron capture detection
GC = gas chromatography
HECD = Hall electron capture detection
MS = mass spectrometry

trans 1,3-dichloropropene are 5 ppb for water samples and 5 ppb for soil and sediment samples in this monitoring program.

For the most part, soil and sediment samples are analyzed in a similar manner to water samples, with the exception that a small amount of water is added to soil and sediment samples. At this point, all three matrices are subjected to a purge-and-trap cycle. An inert gas is bubbled through the sample, volatilizing 1,3-dichloropropene. The gas stream is then passed though an adsorbent tube, which recollects the 1,3-dichloropropene. The sorbent tube is attached to a GC, heated, and backflushed with an inert gas to desorb the halocarbons onto a GC column. Quantification can be accomplished using either a flame ionization detector or an MS, depending on the total concentration of organics in the sample.

EPA's Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (EPA 1982) and Test Methods for Solid Waste (EPA 1986a) are very similar to those already outlined. However, the purge-and-trap cycle may be bypassed for aqueous process wastes with expected concentrations in excess of 10,000 µg/L. In these instances, the sample may be directly injected into the GC system with a 10 mL syringe (EPA 1986a). No other standardized methods for determining 1,3-dichloropropene in environmental samples were located.

It is important to note the discrepancies in detection limits between the standardized methods. CLP cites a detection limit of 5 ppb, yet gives no information regarding the percent recoveries (EPA 1988a). The U.S. EPA procedures for solid wastes (EPA Method 8010) and municipal and industrial waste waters (EPA Method 601), however, maintain a detection limit of 0.34 ppb. The percent recovery, according to the Solid Waste Manual, ranges from 22 to 178 (EPA 1986a). Therefore, results from EPA Method 8010 must be interpreted with caution. For municipal and industrial waste waters, the average percent recoveries for the cis- and trans-isomers are reportedly 86.7 and 73.5 with standard deviations of 6.0 and 17.2%, respectively (EPA 1982). Again, the precision at which the trans-isomer can be measured is questionable

No other standardized methods for the detection of 1,3-dichloropropene in environmental samples were located. However, a few methods have appeared in the available literature. Leiber and Berk (1984) outlined a method for determining 1,3-dichloropropene in ambient air. Tenax-GC sampling tubes are used for sample collection. Solvent desorption is accomplished with isooctane containing 4.0 µg/L of 1,3,5-tribromobenzene, followed by heat treatment at 90°C for 15 minutes; the mixture is then left to stand for 12 hours. After centrifugation, an aliquot of the resulting solution is injected onto the GC column. Sample analysis by capillary GC/ECD was validated for the range of 0.4-4.0 ppm, with a mean percent recovery of 100. Table 6-2 summarizes the methods for detecting cis- and trans-1,3-dichloropropene in environmental media.

TABLE 6-2. Analytical Methods for Determining 1,3-Dichloropropene in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Adsorb (Tenax-GC); desorb (isooctane); inject aliquot	GC/ECD	2.3 mg/m^3	98	Leiber and Berk 1984
Water	Purge and trap	GC/FID GC/MS (EPA CLP Method)	5 ppb	No data	EPA 1988
Water	Purge and trap	GC/MS (EPA Method 8010)	0.34 ppb	22-178	EPA 1986a
Wastewater	Purge and trap	GC/MS (EPA Method 601)	0.20 ppb 0.34 ppb	86.7(cis) 73.5(trans)	EPA 1982
Soil	Add water, heat to 40°, purge and trap, thermal desorption	GC/FID GC/MS (EPA CLP Method)	5 ppb	No data	EPA 1988
Sediment	Add water, heat to 40°, purge and trap, thermal desorption	GC/FID GC/MS (EPA CLP Method)	10 ppb	No data	EPA 1988

ECD = electron capture detector
FID = flame ionization detector
GC = gas chromatography
MS = mass spectrometry

6.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA as amended directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of 1,3-dichloropropene is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of 1,3-dichloropropene.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.3.1 Data Needs

Methods for Determining Biomarkers of Exposure and Effect. There are no known biomarkers of exposure that are unique to 1,3-dichloropropene. Therefore, standardized analytical methods for their determination are not warranted.

There are no known biomarkers of effect that are unique to 1,3-dichloropropene. Therefore, standardized analytical methods for their determination are not warranted.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods for determining of 1,3-dichloropropene in environmental matrices have appeared in the literature. Of these, standardized methods exist only for the analysis of surface water, soil, or sediment samples (EPA 1982, 1986a, 1988). For sediments and soils, the levels of accuracy have not been reported. Both the accuracy and precision at which the trans-isomer can be measured in water is questionable. Therefore, refinement of the current procedures and establishing standardized methods for analyzing other media such as air will aid in determining levels of human exposure to 1,3-dichloropropene.

A limited number of methods is available to determine 1,3-dichloropropene in biological materials (Daft 1989; Kastl and Hermann 1983)‘ and none of the methods have been standardized. The establishment of standardized methods for determining of 1,3-dichloropropene in biological materials, together with methods that are unique to 1,3-dichloropropene exposure, would be helpful in determining the levels of and exposure to the general population.

6.3.2 On-going Studies

The Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, is developing methods for the analysis of 1,3-dichloropropene and other volatile organic compounds in blood. These methods use purge and trap methodology and magnetic mass spectrometry which gives detection limits in the low parts per trillion range.

Other on-going studies developing new analytical methods for determining 1,3-dichloropropene in environmental matrices and/or biological materials were not located.